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(54) GLAZE FOR CERAMIC MASSES

(71) We, KOMBINAT VEB KERAMISCHE WERKE HERMSDORF, of 79, Friedrich-Engels-Strasse, Hermsdorf/Thüringen, German Democratic Republic, a Corporation organised under the laws of the German Democratic Republic, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

The present invention is concerned with a lead-free glaze for ceramic masses, especially for sintered corundum, steatite or stoneware, the glaze beng produced with the use of boron silicate frits.

A lower melting point can generally be achieved by a combination of alkali metal oxides, alkaline earth metal oxides and zinc oxide and by boron trioxide and titanium dioxide. It is also known to add lithium oxide to these glazes. However, these frits have a high coefficient of thermal expansion.

Either the frits contain more alkali metal oxides and very little aluminium trioxide, and then give a glaze with a low melting point and high thermal expansion, or they have a high proportion of aluminium trioxide and silicon dioxide and then give a high melting glaze with a low thermal expansion.

For the last-mentioned lead-free glazes, which are produced with the use of boron silicate frits and have a relatively low coefficient of thermal expansion, the following Seger formula range is known:

0.00—0.20 ZnO
0.30—0.70 CaO
0.00—0.30 MgO . 0.10—0.50 Al_2O_3. 1.50—3.50 SiO_2
0.25—0.30 K_2O 0.00—0.40 TiO_2
0.05—0.15 Na_2O 0.35—0.90 B_2O_3

The stoving temperatures of these glazes is, however, about 1000°C.

In general, these glazes only fulfil the function of providing a smooth and glossy surface. Therefore, the requirement for an economic production consists in the achievement of a saving of energy and a shortening of the production time at a low fusion temperature and with a short melting time, with a low coefficient of thermal expansion adapted to the ceramic bodies to be glazed.

The known glazes for such ceramic masses either contain lead or are produced with the use of a boron silicate frit.

However, in both cases, the glaze either has a fusion temperature of about 1000°C. and too low a coefficient of thermal expansion or has too high a coefficient of thermal expansion and melts at a lower fusion temperature.

In the case of known lead-free glazes, the limiting values for frits which contain sodium oxide, potassium oxide, calcium oxide, boron trioxide, aluminium trioxide and silicon dioxide lie within the following range:

0.3—0.7 Na_2O and/or K_2O up to 0.1 Al_2O_3 up to 3.0 SiO_2
0.7—0.3 CaO up to 1.0 B_2O_3

It is, therefore, an object of the present invention to coordinate the low coefficient of thermal expansion of the ceramic masses with a flux-rich base glaze, dictated by a low stoving temperature.

Therefore, the problem forming the basis of the present invention is to provide a lead-free glaze for ceramic masses, especially for sintered corundum, steatite or stoneware, produced with the use of boron silicate frits, which melts at temperatures of about 800°C.

and has a coefficient of thermal expansion at this temperature which is adapted to the ceramic bodies to be glazed.

Thus, according to the present invention, there is provided a glaze for ceramic bodies produced from one or more boron silicate frits, wherein the glaze lies within the following Seger formula range:

0.3—0.7 Na_2O and/or K_2O
0.1—0.6 CaO
0.0—0.3 ZnO . 0.2—0.4 Al_2O_3. 1.5—4.0 SiO_2 0.5—3.0 B_2O_3
0.0—0.2 MgO
0.05—0.2 BaO

It is to be understood that the lead-free glaze according to the present invention is produced from one or more frits of the alkali metal-, alkaline earth metal-, zinc- or barium-containing aluminoborosilicate types of frits which, for the sake of simplicity, are herein referred to as boron silicate frits. The use of the term in the plural is because, within the given limits in the Seger formula range, there can be several frits suitable for the intended purpose. It is also to be understood that the glaze can be produced not only from one but also from several frits within the given Seger formula range.

It is also preferable for the glaze to contain up to 2% by weight lithium oxide and/or up to 5% by weight titanium dioxide as components of the Seger formula.

For the preparation of the glaze, it is preferable not to add clay or kaolin to the components during grinding thereof but to add up to 1% by weight bentonite and/or up to 0.15% by weight calcium chloride to the components of the glaze.

The new glaze according to the present invention has a coefficient of thermal expansion of $\alpha_{11n}=5-7\times10^{-6}$. °C.$^{-1}$ at about 800 °C. fusion temperature and about 45 minutes melting time. It melts to give a transparent material and readily develops the colours under the glaze. Insofar as no special technical requirements are demanded of the vitreous coating, the introduction of the glazes into the production is of considerable economic usefulness.

The present invention is illustrated in the following on the basis of two specific Examples, the given batches having been previously fritted. The glazes are prepared and applied in a manner conventional in ceramic processes but, because of the low melting temperature and the short melting time, without the addition of clay or koalin to the grinding batch.

The consistency of the workable glaze material is solely brought about by the addition of 0.5% by weight, Hungarian bentonite and 0.03% by weight calcium chloride in an aqueous grinding up of the frit powder.

Both of the following Examples show that it is an important feature of the present invention that the amphoteric and acidic molar proportions in the Seger formula are selected so as to be as high as possible.

Example 1

0.55 Na_2O/K_2O	
0.10 ZnO	3.2 SiO_2
0.20 CaO . 0.35 Al_2O_3	
0.10 BaO	1.5 B_2O_3
0.05 MgO	
fusion temperature	800°C.
melting time	45 minutes
coefficient of thermal expansion	$\alpha_{11n}=64.36\times10^{-7}$. °C.$^{-1}$
surface tension	292.33 dyn/cm.

Example 2

0.5 Na_2O	
0.1 Li_2O	3.5 SiO_2
0.2 ZnO 0.35 Al_2O_3	
0.1 BaO	2.0 B_2O_3
0.1 CaO	
fusion temperature	820°C.
melting time	45 minutes
coefficient of thermal expansion	$\alpha_{11n}=56.8\times10^{-7}$. °C.$^{-1}$

The addition of small amounts (for example 0.7% by weight) of lithium oxide to the above-described glazes has a favourable effect. Especially in the case of small amounts of lithium oxide, an unmistakeable melt-promoting action occurs, the coefficient of

thermal expansion thereby being reduced by increased quartz dissolving and a good surface and increased gloss being produced. Furthermore, up to 5% by weight titanium dioxide can be added to the batch for increasing the melt flux.

WHAT WE CLAIM IS:—

1. A clear, transparent lead-free glaze for ceramic bodies produced from one or more boron silicate frits, wherein the glaze lies within the following Seger formula range:

$$\frac{\begin{matrix}0.3\text{—}0.7\ Na_2O \text{ and/or } K_2O \\ 0.1\text{—}0.6\ CaO \\ 0.0\text{—}0.3\ ZnO \\ 0.0\text{—}0.2\ MgO \\ 0.05\text{—}0.2\ BaO\end{matrix}}{0.2\text{—}0.4\ Al_2O_3} \quad \frac{1.5\text{—}4.0\ SiO_2}{0.5\text{—}3.0\ B_2O_3}$$

2. A lead-free glaze according to claim 1, wherein it additionally contains up to 2% by weight lithium oxide as a component of the Seger formula.

3. A lead-free glaze according to claim 1 or 2, wherein it additionally contains up to 5% by weight titanium dioxide as a component of the Seger formula.

4. A lead-free glaze according to any of the preceding claims, wherein the components of the glaze have been ground in the presence of up to 1% by weight bentonite and/or up to 0.15% by weight calcium chloride.

5. A lead-free glaze according to claim 1, substantially as hereinbefore described and exemplified.

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